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A DFT Study of Electronic Structures on Hydrated Sulfate Clusters $[SO_4^{2-}(H_2O)_n]$ n = 0–4, 16

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Abstract - Micro-hydrated Hofmeister ions have always become the center of research interest while studying the influence of hydration on geometries of hetero-atom centered ions by both experimental and theoretical techniques. The inorganic divalent sulfur-centered anion SO_4^{2-} is one of such ions that is ranked first among the anions in Hofmeister series. Being this anion as a major component in many electrolytic solutions and sea water as well as in biosynthesis of active sulfate and in laxatives drugs, understanding how an isolated SO_4^{2-} undergoes solvation and structural stabilization electronically is indispensable. This study is aimed to probe deep into the molecular-level of the SO_4^{2-} ion hydration by applying ab initio type theoretical calculations. It is found that whenever the solvent number n = 1 to 4 H_2O, the SO_4^{2-} attracts H_2O strongly enough that two H–bonds are formed with each H_2O, and when n > 4 H_2O (in this case, $[SO_4^{2-}(H_2O)_{16}]$), the SO_4^{2-} forms single H–bond with H_2O that is further bonded to another H_2O by H–bonds. Interestingly, no significant geometric distortion of the central SO_4^{2-} ion is observed in its hydrated form. It is believed that this computational study will not only ease to learn most of the physicochemical properties of SO_4^{2-} ions in any inorganic sulfate solutions (including in human body fluids), but also to model their hydrated systems while exploring solvation dynamics in bulk solutions.

Keywords - Hofmeister ions, Hydrated sulfate clusters, Electrostatic potential surface (ESP) map, and DFT optimization.

I. INTRODUCTION

Hydration of ions, though concerns a great deal of information, is mostly referred to the number of water molecules that are coordinated to the ions and much concern is their distribution and bound state around the ions. In experimental research, advanced instrumentation techniques such as IR [1], NMR [2], Raman spectroscopy [3], Neutron diffraction [4], and Gel exclusion chromatography [5] etc. are most commonly used to study ionic hydration and hydration structures. However, in theoretical/computational research, advanced mathematical calculations such as energy minimization (also called energy or geometry optimization) techniques are used to compute the equilibrium configuration of the hydrated ions. Such techniques precisely locate minimum energy confirmation from the initial structure of the hydrated ionic specimen by a series of computing process or repeated mathematical calculations [6]. This computational procedure involves calculation of the wave function and energy at a starting hydrated ionic confirmation and then, proceeding to search the nearest minimum energy confirmation using the smallest number of calculations possible. Thus, in computational/theoretical research, the energy minimization methodology, that generates atomic Cartesian coordinates of the most stable electronic structures of the hydrated ions, dimensions of the optimized parameters such as atomic/ionic and ion-water distances and angles [7], is frequently used to find a route from a trial structure to the global minimum structure (ground state electronic structure). In order to implement such powerful computational methodology, an electronic structure package known as *Gaussian* has been offering the wide verities of computational models [7]. A density functional theory (hereafter, DFT) model is one of them. It is a renowned quantum mechanical model for investigating ground state

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electronic structures of the multi-electron homo-/hetero-atomic ionic systems with and without hydrated forms [8], [9], [10], in spite of its many notable limitations while applying to large molecular/atomic assemblies [11]. Even though it includes a formalism for approximately solving Schrodinger's wave equation, it produces better results than *ab initio* electronic structure methods at the similar computational cost [12], [13].

According to dissolution theory, solubility of the ionic compounds in the universal solvent such as water is a characteristic property of them but their ionization that is followed by dissolution in the aqueous solution is a very strange phenomenon. One of the main strange features of the dissolved ions is their nearly independent existence to one another in the aqueous solution. The resolution of this independency lies in the interactions between ions and the water molecules. As oxygen atom of a H_2O molecule has a higher electronegativity (χ_O = 3.5 in Pauling scale) than hydrogen atoms (χ_H = 2.1), an O and two H atoms must act as negative and positive terminals respectively and hence, creating an electric dipole in the H_2O molecule. As a result, the positive and negative ions in the aqueous solution are attracted towards the negative and positive terminals of the dipolar H_2O molecule respectively. Such ion-dipole attractive force leads to the formation of water clusters around the immediate vicinity of positively and negatively charged ions. This phenomenon is more commonly called hydration (solvation). Many homo-atomic (Ca^{2+}, Cl^{-}, Mg^{2+}, V^{2+}, Cu^{2+} etc.)/hetero-atomic (SO_4^{2-}, NO_3^{-}, PO_4^{3-}, HSO_4^{-} etc.) electropositive and electronegative radicals undergo hydration in the aqueous solution with distinct hydration number [14]. Among them, hydration of sulfate ions has captivated many researchers as they are ranked first among the anions in Hofmeister series due to having strong ability to decrease protein solubility.

Being one of the major components of sea water (885 mg/L) and existing in the different sized clusters of the form $[SO_4^{2-}(H_2O)_n]$, $n \leq 50$ [15], the hydrated SO_4^{2-} ions not only affect the distillation desalination method by slowing down the osmosis process (due to bigger sized clusters) through the permeable membranes [16] but also cause excessive water flow due to their migration through ion exchange membrane in the flow battery systems where oxidized and reduced form of the inorganic sulfate compounds are used as catholyte and anolyte respectively [17]. In human body, SO_4^{2-} ions which are very essential in the biosynthesis of active sulfate (3'- phosphoadenosine-5'-phosphosulfate (hereafter, PAPS)) are produced as a result of protein turnover, degradation of excess protein-derived amino acids, and metabolism of several organic and inorganic sulfur compounds present in food and water [18]. As the unhydrated SO_4^{2-} ions are very unstable and the adult human body is composed of 50-65% water, the SO_4^{2-} ions inside the human body get very favorable environment for clustering with H_2O molecules $[SO_4^{2-}(H_2O)_n]$. And it is an extremely essential process without which SO_4^{2-} ion gastrointestinal absorption, biosynthesis of PAPS, and the concerned metabolic processes won't be eased. Furthermore, such hydrated forms of sulfate or inorganic sulfate compounds are also present in (i) beverages such as beer, cider, cola, juice, milk (coconut, human, animal, and infant formula), wine, mineral and distilled water etc.; (ii) foods and vegetables such as almonds, broccoli, bread, cauliflower, dried fruits, sausage, peanuts etc.; (iii) soils (850 mg/kg); (iv) laxatives (Na_2SO_4 solution) that are used to clean out patients' bowel during medical treatments [19].

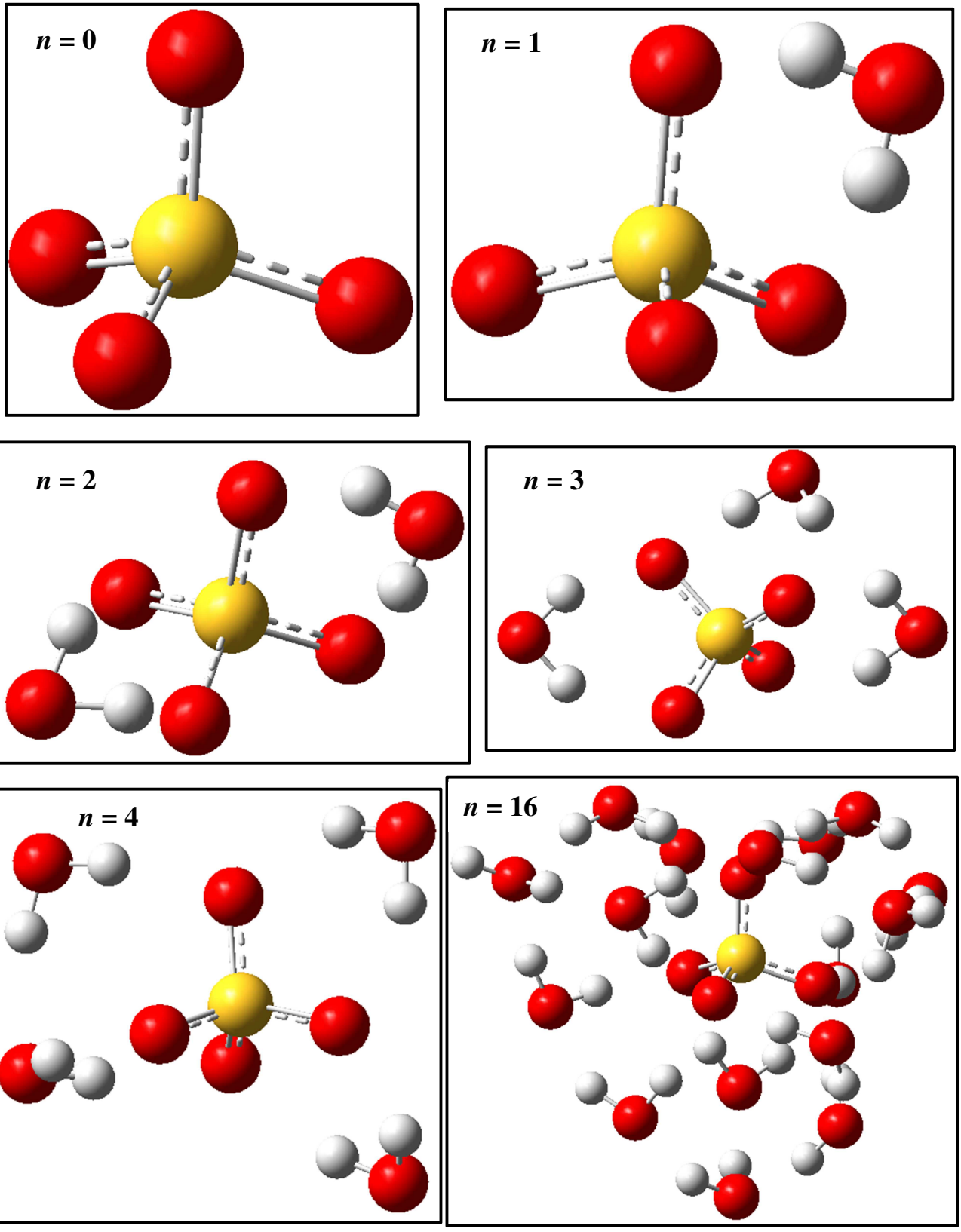
Being such a useful and an essential inorganic ions which have become an important part of our growth and survival, in-depth investigation about their stabilization by variable number of water molecules clustering around them and their mutual interactions in the aqueous solution is very crucial. As a rule, when the water molecules around sulfate radical move closer to latter under the influence of their mutual attractive force, change in total electronic energy of the microscopic particles takes place. It should be evaluated properly by some means in order to explore the chemistry of the hydrated sulfate structures in its aqueous solution. Even though, Smeeton *et al.* has already applied *basin-hoping Monte Carlo* method to different sized hydrated sulfate clusters $[SO_4^{2-}(H_2O)_n]$, $n \leq 50$ [15], it is regarded as a less computationally demanding method for computing low energy electronic structures. Therefore, comparatively more accurate *ab initio* type methodology could be one of the best alternative theoretical models to compute change in total electronic energies of the hydrated sulfate systems while relaxing all the surrounding water molecules and the central sulfate ion. In this study, a DFT model is applied explicitly to $[SO_4^{2-}(H_2O)_n]$, n = 0–4, and 16 (as optimizing more bigger clusters by *ab initio* type method is computationally expensive) and produced their respective global minimum electronic structures. The $[SO_4^{2-}(H_2O)_{16}]$ is chosen here as a representative sulfate-water cluster among the bigger clusters as photoemission [20] and FTIR [21] spectroscopies have already revealed that sulfate ions usually form a stable hydration shell consisting 16 water molecules. It is believed that the present theoretical calculations have unveiled an extensive knowledge for explaining at least stabilization phenomena of SO_4^{2-} ions by variable number of water

molecules and their mutual interactions in the aqueous solution. The structure of this paper is as follows. The computational methods are outlined in section 2, results and discussions are presented in section 3, and summary and conclusions are given in section 4.

II. COMPUTATIONAL METHODS

At first, a trial structure of the divalent SO_4^{2-} radical with four oxygen atoms and a central sulfur atom in two dimensional axis was built by using GaussView visualization application software [22] and then nH_2O molecules (n = 1, 2, 3, 4) were added to its immediate vicinity one molecule at a time to construct the trial structures of $[SO_4^{2-}(H_2O)]$, $[SO_4^{2-}(H_2O)_2]$, $[SO_4^{2-}(H_2O)_3]$, and $[SO_4^{2-}(H_2O)_4]$. However, due to computational complexity, the trial structure of $[SO_4^{2-}(H_2O)_{16}]$ ion was directly displayed by using the Cartesian coordinates extracted from the database file produced by the Monte Carlo simulation method [15]. An 'n' = 0, 1, 2, 3, 4, and 16 indicates unhydrated, monohydrated (1 molecule equivalent of water), dihydrated (2 molecules equivalent of water), trihydrated (3 molecules equivalent of water), tetrahydrated (4 molecules equivalent of water), and hexadecahydrated (16 molecules equivalent of water) SO_4^{2-} ions, as shown in chart 1. These initial structures of the unhydrated and four different hydrated sulfate ions have each S−O bond length 1.670Å, each O−H bond length 0.840Å, each O−S−O bond angle 109.472°, and each H−O−H bond angle 96.9957°. The oxygen atoms of the SO_4^{2-} unit in each trial structure were left unbound to surrounding H_2O molecule/s in order to realize latter as hydrated water molecules computationally. The initial atomic Cartesian coordinates for $[SO_4^{2-}(H_2O)_n]$, n = 1 to 4 were extracted from the respective trial structures. The x, y, and z coordinates of each ionic specimen were used manually to prepare *Gaussian* input files separately for the purpose of computing low energy structures. All the *Gaussian* keywords and methodologies were selected as instructed in *Gaussian* 09 manual [23]. The hybrid functional based DFT method known as B3LYP was used with the basis set of this type: *6−31G (d, p)* i.e. the methodology used was DFT: *B3LYP / 6−31G (d, p)*. In order to solve the electronic Schrodinger equation iteratively, the self-consistent field (SCF) with both default SCF procedure (*SCF=Tight*) and Berny algorithm for optimizations to a local minimum were selected in *Gaussian* 09 [24]. The *Gaussian* output files such as *log*, checkpoint (*.chk*), and formatted checkpoint (*.fchk*) files were read by using the *Gaussian* graphical interface i.e. GaussView and various chemical data displayed in three dimensions were extracted. And then, the optimized ground state electronic structures, optimized parameters such as bond lengths and bond angles, electron density surface (ESP mapping) for each hydrated sulfate cluster $[SO_4^{2-}(H_2O)_n]$, n = 0−4,16 were analyzed thoroughly.

Chart 1: Trial structures of hydrated sulfate $[SO_4^{2-}(H_2O)_n]$, n = 0-4,16



III. Results and Discussion

3.1. Ground state electronic structures

3.1.1 Naked SO_4^{2-} ion $[SO_4^{2-}(H_2O)_0]$

The unhydrated SO42- ion i.e. [SO42−(H2O)n], n = 0 can be called naked SO42− ion due to the absence of water molecules in its immediate vicinity. Despite the inexistence of SO42− ion in nature in an isolated and unhydrated form, its ground state electronic structure is presented here in order to explore the effect of hydration on its geometry and electronic stability. The DFT optimized geometry of unhydrated sulfate is shown in Figure 1a, where yellow spheroid represents Sulphur (S) atom and red spheroids represent Oxygen (O) atoms. As the optimized geometry is specified mostly in terms of the three parameters namely bond length: an average distance between the nuclei of two atoms bonded together in any given molecule; bond angle: angle formed between three atoms across the two bonds; and torsional angle: angle between the plane formed by the first three atoms and the plane formed by the last three atoms, the explicitly measured theoretically calculated values of the first two parameters are listed as: each S–O bond length is 1.52 Å, and each O–S–O bond angle is 109.5°. As SO42− has altogether 5 atoms with 6 valence electrons each (6 valence electrons ×5), and 2 negative charges, there are total 32 electrons i.e. 16 electron pairs that are to be distributed over 5 centers. The least electronegative S atom is at the center and, when it forms two double bond with any two O atoms (octet rule), it should form single bond with remaining two O atoms. There are 8 electrons around the doubly bound oxygen atoms, 6 valence electrons, and 2 inner core electrons, and thus these oxygens are neutral, because they got 8 protons in their nuclear core. Around sulfur, there are 6 valence electrons, and 10 inner core electrons, and thus for atomic number (Z) = 16, the sulfur atom is neutral. But around each singly bound oxygen atoms, there are 9 electrons, i.e. 2 inner core, one from the S–O single bond, and 6 from the oxygen valance electrons and given these 9 electrons and a Z = 8 nuclear charge, these oxygens are formal anions. In order to minimize the ground state electronic energy, this divalent sulfate ion SO42− delocalizes its electron density, and such way of spreading out electron density is usually represented by its resonance hybrid structure as shown in Figure 1a. It is obvious that the bond lengths in the resonance hybrid should be an average of the bond lengths in the separate resonating contributors. Therefore, the resonance hybrid structure of Figure 1a has each O–S bond equal in length i.e. 1.52 Å. It also justifies why the O–S bond length in naked sulfate ion is shorter than the O–S bonds (1.57 Å) and longer than the O=S bonds (1.42 Å) of H2SO4 where two of the single bonded O hold H. As there are four electron pairs around the central S atom, the sulfate ion must assume the shape of a regular tetrahedron with each ∠O–S–O = 109.5° if we refer

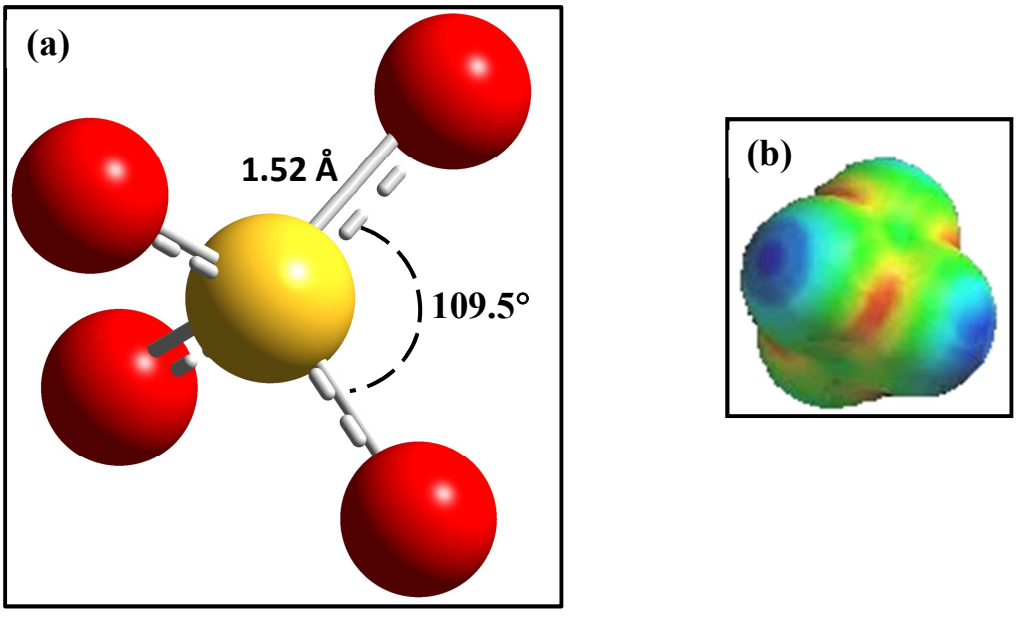


Figure 1. (a) DFT optimized geometry and (b) Electron density surface (ESP mapping) of SO_4^{2-} ion. For simplicity, formal charge of the sulfate ion is not shown.

the assumption of valence shell electron pair repulsion (VSEPR) theory. Similarly, according to valence bond theory (VBT), the tetrahedral geometry of sulfate ion is due to the presence of SP3 hybridized S atom at the center. This is dictated by the fact that S needs to form bonds to four O atoms in a molecule of tetrahedral symmetry. In addition to this, π bonds that are formed by the electrons in the non-bonding p atomic orbitals on oxygen with the sulfur atom's empty d orbitals are interchanged by resonance and the net result is similar to previously depicted DFT derived Lewis resonating hybrid structure of Figure 1a. The tetrahedral orientation of the four oxygen atoms in SO42− ion can be reconfirmed by looking at its DFT derived three dimensional model of the electrostatic potential (ESP) map shown in Figure 1b, where the four spherical protrusions that emerge from the central region (central atom: S) represent particular alignment of the oxygen atoms around the central sulfur atom.

3.1.2 Monohydrated sulfate ion [$SO_4^{2-}(H_2O)$]

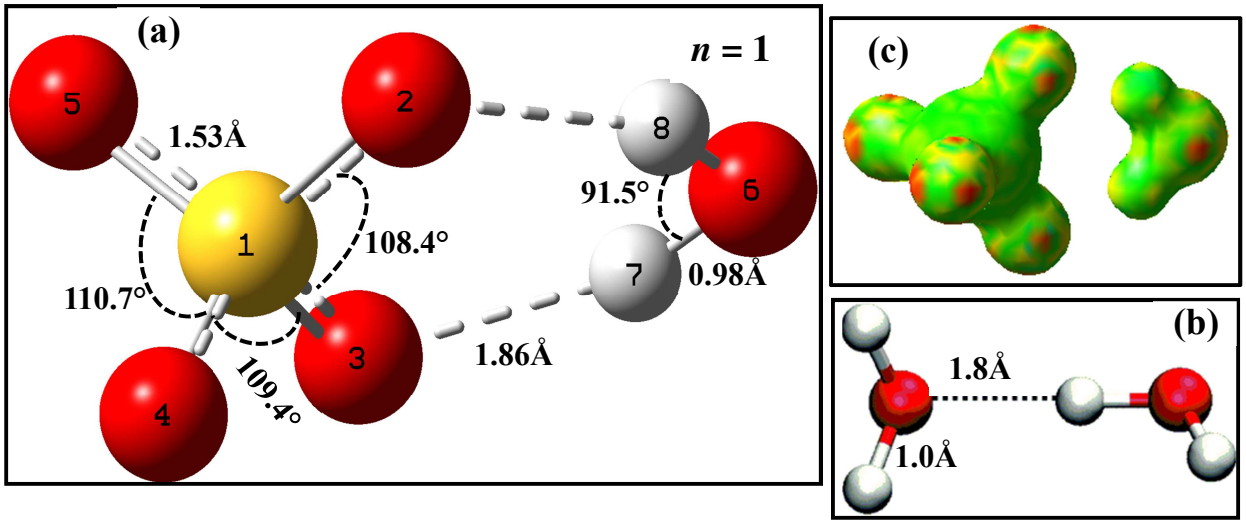


Figure 2. (a) DFT optimized geometry of [$SO_4^{2-}(H_2O)$] ion, (b) Intermolecular space in bulk water, and (c) Electron density surface (ESP mapping) of [$SO_4^{2-}(H_2O)$] ion. For simplicity, formal charge of the sulfate ion is not shown.

The monohydrated SO42− ion i.e. [SO42−(H2O)n], n = 1 has one molecule equivalent of water in the immediate vicinity of the SO42− ion. The DFT optimized geometry of it is shown in Figure 2a, where yellow spheroid represents Sulphur (S) atom, red spheroids represent Oxygen (O) atoms, and ash grey spheroids represent Hydrogen (H) atoms. The explicitly measured theoretically calculated dimension of the bond lengths are listed as: each S−O bond length is 1.53 Å (naked sulfate ion: S−O bond length is 1.52 Å), each O–H bond length is 0.98 Å and each H-----O hydrogen bond length is 1.86 Å. It indicates no significant changes in S−O bond length while hydrating SO42− ion with one molecule equivalent of water even though two of the four O atoms are linked with the two separate H atoms of H2O molecule by comparatively weaker hydrogen bond (hereafter, H–bond), as shown in Figure 2a. Interestingly, lengths of the both H–bonds and O–H bonds are as equal as the length of the H–bond between the water molecules i.e. equal to intermolecular space and the two O–H bond lengths of each H2O molecule in bulk water system respectively as shown in Figure 2b. However, the original O–S–O bond angle (109.5°) of naked sulfate ion is changed to 108.4° and 110.7°; and an H–O–H bond angle in H2O is reduced to 91.5° from its original value 104.5° as indicated in the DFT optimized geometry. A small difference (~1°) in the angular value is observed in the O–S–O bond angle facing towards hydrated water molecule. This is simply due to the bound state of the two O atoms of this bond angle through the hydrogen bonds (the two negative charges on SO42− attract H2O molecule strongly enough that two H–bonds are formed to each other) that may fix their positions in the three dimensional space and hence, may direct them at the specific direction. It ultimately affects the opposite O–S–O bond angle and causes latter to deviate from the original value. The reverse is true for bound H2O molecule which remains in the immediate vicinity of two electronegative O

atoms of SO42− and occupies its specific position restricted by the two H−bonds. That is why, the O−S−O angle of SO42− facing towards immediate H2O molecule may also play an important role to reduce the H−O−H angle and vice versa. As a whole, no significant change in overall geometry of the SO42− ion is observed while hydrating it with one molecule equivalent of water, but little delocalization of charge from former to latter species occur that may be responsible to bind them each other. This explanation is in good agreement with the experimental finding (Photodetachment Spectroscopy) reported by Wang et al.: the first water strongly binds to SO42− by forming two H−bonds with binding energy 27.7 kcal/mol. [25]. An existence of the distinct structural unit of the monohydrated SO42− with minimal distortions in the S−O bond lengths, O−S−O bond angles and ideal tetrahedral structure can also be reconfirmed by looking at the three dimensional model of the electrostatic potential map of SO42− (H2O) shown in Figure 2c, where the four spherical protrusions that emerge from the central region represent alignment of the four oxygen atoms around the central sulfur atom. The actual orientation and location of the H2O molecule in the immediate vicinity of SO42−can also be clearly observed. Such electron density model of the hydrated ion also speculates the binding state between SO42−and an H2O molecule.

3.1.3. Polyhydrated sulfate ions $[SO_4^{2-}(H_2O)_n]$, $n > 1$

3.1.3.1 $[SO_4^{2-}(H_2O)_n]$, $n = 2$, 3, and 4

The dihydrated [SO42−(H2O)n], n = 2; trihydrated [SO42−(H2O)n], n = 3; and tetrahydrated [SO42−(H2O)n], n = 4 sulfate ions have two, three, and four molecule equivalent of water in the immediate vicinity of the SO42− ion respectively. The DFT optimized geometry of dihydrated SO42− ion i.e. [SO42−(H2O)n], n = 2 is shown in Figure 3a, where yellow spheroid represents Sulphur (S) atom, red spheroids represent Oxygen (O) atoms, and ash grey spheroids represent Hydrogen (H) atoms. The explicitly measured theoretically calculated dimension of the bond lengths are listed as: each S−O bond length is 1.52 Å (naked sulfate ion: S−O bond length is 1.52 Å and monohydrated sulfate ion: S−O bond length is 1.53 Å), each O−H bond length is 0.98 Å and each H-bond length is 1.89 Å (monohydrated sulfate ion: H−bond length is 1.86 Å). It indicates no significant changes in S−O bond length while hydrating SO42− ion with two molecule equivalent of water even though all the four O atoms are linked with the four separate H atoms of two H2O molecules by comparatively weaker H−bonds, as shown in Figure 3a. Each oxygen of SO42− ion is found to link with one hydrogen of each H2O molecule forming water cluster of symmetric dimer (C2v). Interestingly, lengths of the all four H−bonds and O−H bonds are as equal as the length of the H−bond between the water molecules i.e. equal to intermolecular space and the two O−H bond lengths of each H2O molecule in bulk water system respectively (Figure 2b). However, the original O−S−O bond angle (109.5°) of naked sulfate ion is changed to 108.5°, equal to monohydrated case; and the H−O−H bond angles in hydrated H2O molecules are reduced to 92.7° (monohydrated has ∠ H−O−H = 91.5°) from its original value 104.5° as mentioned in the DFT optimized geometry. A small difference (~1°) in the angular value is observed in the O−S−O bond angles facing towards two hydrated water molecules. This is simply due to the bound state of the four O atoms through the four H−bonds that may fix their positions in the three dimensional space and hence, may direct them at the specific direction. The reverse is true for bound H2O molecules which remain in the immediate vicinity of four electronegative O atoms of SO42− and occupies their specific position restricted by the four hydrogen bonds. That is why, the O−S−O angles of SO42− facing towards two hydrated H2O molecules may also play an important role to reduce the H−O−H angles and vice versa. Furthermore, the H−bond length measured in dihydrated sulfate ion (1.89Å) is slightly longer than that in the monohydrated case (1.86Å). It is obvious because the former has four H−bonds whereas the latter has two H−bonds though intensity of the negative charges on central SO42− that attracts water molecules towards itself remains unchanged and hence, lesser attractive force is experienced by the two hydrated water molecules of the former ion (i.e. long range bonding interaction) than by the one water molecule present in the latter ion. Like in monohydrated case, no significant change in overall geometry of the SO42− ion is observed while hydrating it with two molecule equivalent of water, except little delocalization of charge from central ion to surrounding water molecules occur that is essential to bind them each other. This theoretical explanation is in good agreement with the experimental finding (Photodetachment Spectroscopy) reported by Wang et al.: each of the two water molecules strongly binds to SO42− by forming two H−bonds with binding energy 26.4 kcal/mol. [25]. The formation of the distinct structural unit of the dihydrated SO42− with minimal distortions in the S−O bond lengths, O−S−O bond angles and ideal tetrahedral structure can also be confirmed by the three dimensional model of the electrostatic potential map of SO42−(H2O)2 shown in Figure 3b, where the four spherical protrusions that emerge from the central region represent alignment of

the four oxygen atoms around the central sulfur atom. The actual orientation and location of the two H2O molecules in the immediate vicinity of SO42− can also be clearly observed reconfirming symmetric dimer structural motif. This sort of electron density model of the hydrated ion also speculates the binding state between central ion and immediate two H2O molecules.

Moreover, the DFT optimized geometries of tri- and tetra- hydrated SO42− ions i.e. [SO42−(H2O)n], n = 3 and 4 are shown in Figure 4a and Figure 5a respectively, where yellow spheroid represents Sulphur (S) atom, red spheroids represent Oxygen (O) atoms, and ash grey spheroids represent Hydrogen (H) atoms. Like in dihydrated sulfate ion, no significant change in geometry of the SO42− ions are observed while hydrating with three, and four molecule equivalent of water in the immediate vicinity of the central SO42− ion except little delocalization of charge from SO42−species to surrounding H2O molecules which is responsible to bind them together. Additionally, all the four O atoms (two O atoms in trihydrated SO42− ion) of tetrahydrated SO42−ion are linked with the eight (four) separate H atoms of four (three) H2O molecules by two H−bonds, as shown in Figure 5a (Figure 4a). It is in good agreement with the experimental finding (Photodetachment Spectroscopy) reported by Wang et al.: each of the three and four water molecules strongly binds to SO42− by forming two H−bonds with binding energy 24.9 kcal/mol. and 23.5 kcal/mol. respectively [25]. As mentioned in the respective DFT derived geometries, both trihydrated, and tetrahydrated structures have an approximately equal length of the H−bonds (1.9Å), which is slightly longer than the H−bond between H2O molecules (1.8Å) in bulk water system shown in Figure 2b.

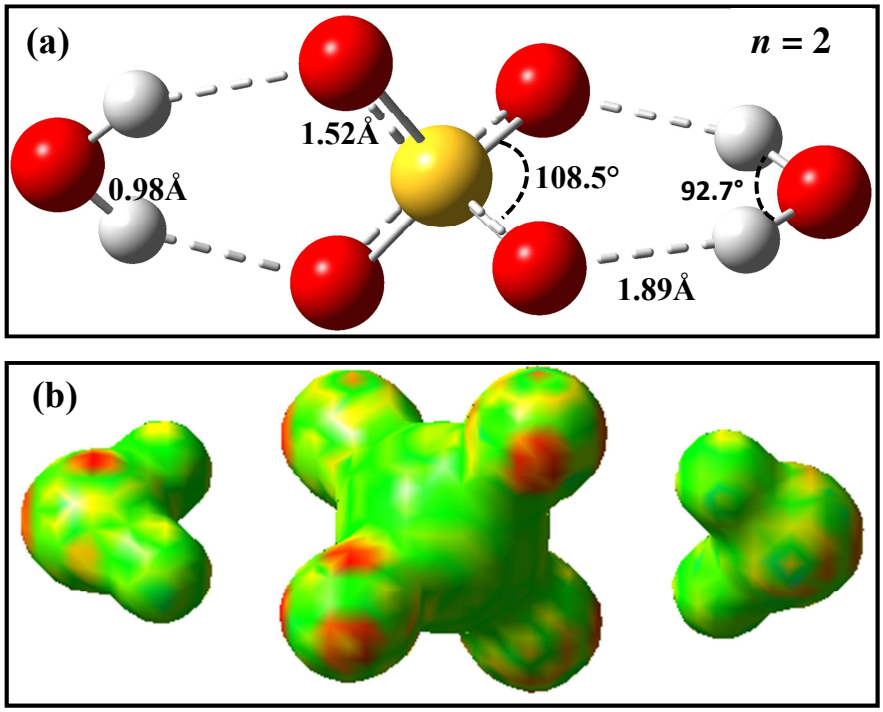


Figure 3. (a) DFT optimized geometry and (b) Electron density surface (ESP mapping) of $[SO_4^{2-}(H_2O)_2]$ ion. For simplicity, formal charge of the sulfate ion is not shown.

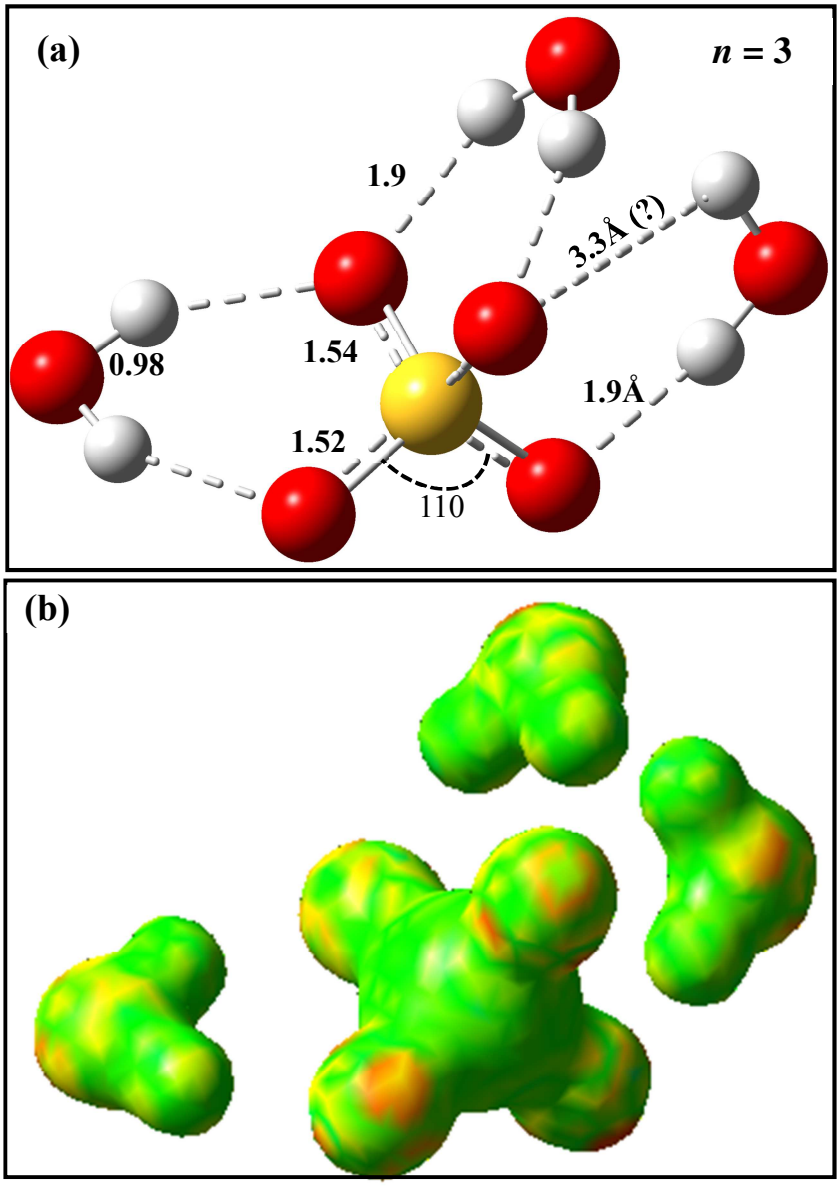


Figure 4. (a) DFT optimized geometry and (b) Electron density surface (ESP mapping) of $[SO_4^{2-}(H_2O)_3]$ ion. For simplicity, formal charge of the sulfate ion is not shown.

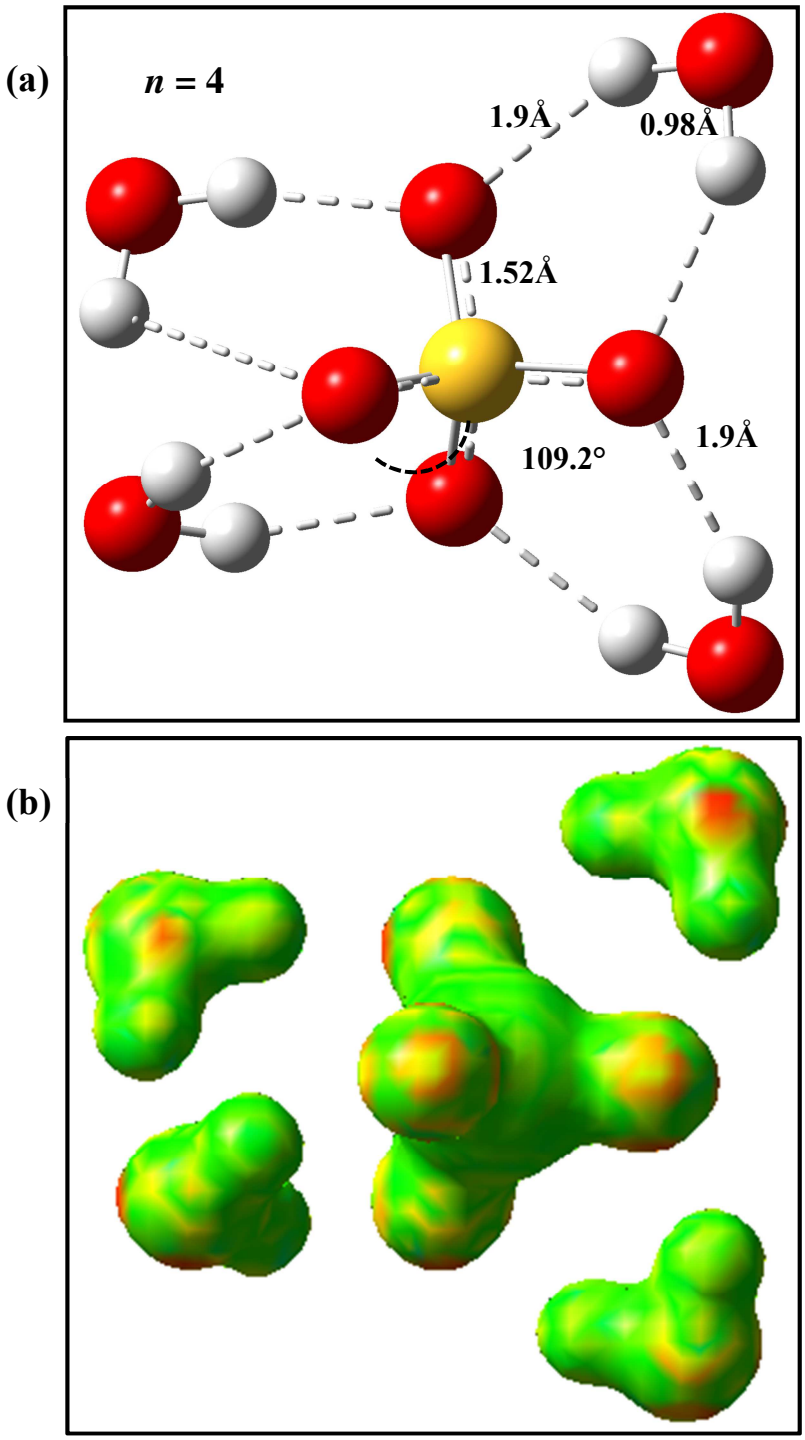


Figure 5. (a) DFT optimized geometry and (b) Electron density surface (ESP mapping) of $[SO_4^{2-}(H_2O)_4]$ ion. For simplicity, formal charge of the sulfate ion is not shown.

In conclusion, as in the monohydrated sulfate ion, where first water strongly binds to SO42− forming two strong H−bonds, the second, third, and fourth H2O also form two strong H−bonds each with central SO42− ion as seen clearly in the DFT derived ground state electronic structures of dihydrated, trihydrated, and tetrahydrated geometries shown in Figure 3a, Figure 4a, and Figure 5a respectively. Thus, in SO42−(H2O)3 each of the two oxygen on SO42− is bonded

to two H2O (each of the remaining two oxygen on SO42− is bonded to one H2O), forming an asymmetric solvated cluster of cyclic trimer, whereas in SO42−(H2O)4, each oxygen on SO42−is bonded to two H2O, forming a symmetric solvated cluster (C2v) of cyclic tetramer. An existence of the tetrahedral structural motifs with the symmetric and asymmetric hydrated structures can also be confirmed by looking at the three dimensional model of the electrostatic potential map of [SO42−(H2O)n], n = 3 and 4, shown in Figure 4b and Figure 5b respectively, where the four spherical protrusions that emerge from the central region represent alignment of the four oxygen atoms around the central sulfur atom. The actual orientation and location of the H2O molecules in the immediate vicinity of SO42− can also be clearly observed. This electron density model of the hydrated ions also speculates the binding state between SO42− and immediate H2O molecules.

3.1.3.2 $[SO_4^{2-}(H_2O)_n]$, $n = 16$

From the above results and discussions for the smaller sulfate ion hydrated clusters, it is expected that larger clusters such as SO42−(H2O)n, n > 4 would also attain tetrahedral structural motifs with all H2O double H−bonded to SO42−. However, the basin-hopping Monte Carlo method [15] predicted that the lowest energy structures of larger clusters have only few H2O double H−bonded to SO42− and the rest forms cyclic structure, with each H2O donating one H to H2O and one to SO42−. As can be seen in the DFT derived [SO42−(H2O)4] structure (Figure 5), the delocalization of negative charges from the central SO42− species to surrounding four H2O molecules must be maximum rather than in the smaller clusters. This is due to the symmetric

orientation of the four water molecules exactly towards the direction of the four O atoms of central SO42− ion. If the solvent number increases from four (n > 4), there is sufficient chance of screening negative charges on SO42− by immediate water molecules so that single H−bonds, with H2O−H2O interactions will be favored. The same is the result appeared in the DFT optimized ground state electronic structure of the representative bigger cluster such as [SO42−(H2O)16] as shown in Figure 6(a). Even though the H−bonds formed between H2O and central SO42− and H2O and H2O are not shown in the structure for simplicity, the intermolecular space between outer circle H2O molecules (farthest = 1.3 Å) and the space between central SO42− ion and inner circle H2O molecules (farthest = 1.5Å) are so close to each other that the H−bonds formation will be favorable. This is clearly visible in the electrostatic potential map of [SO42−(H2O)16], shown in Figure 6(b), where the four spherical protrusions that emerge from the central

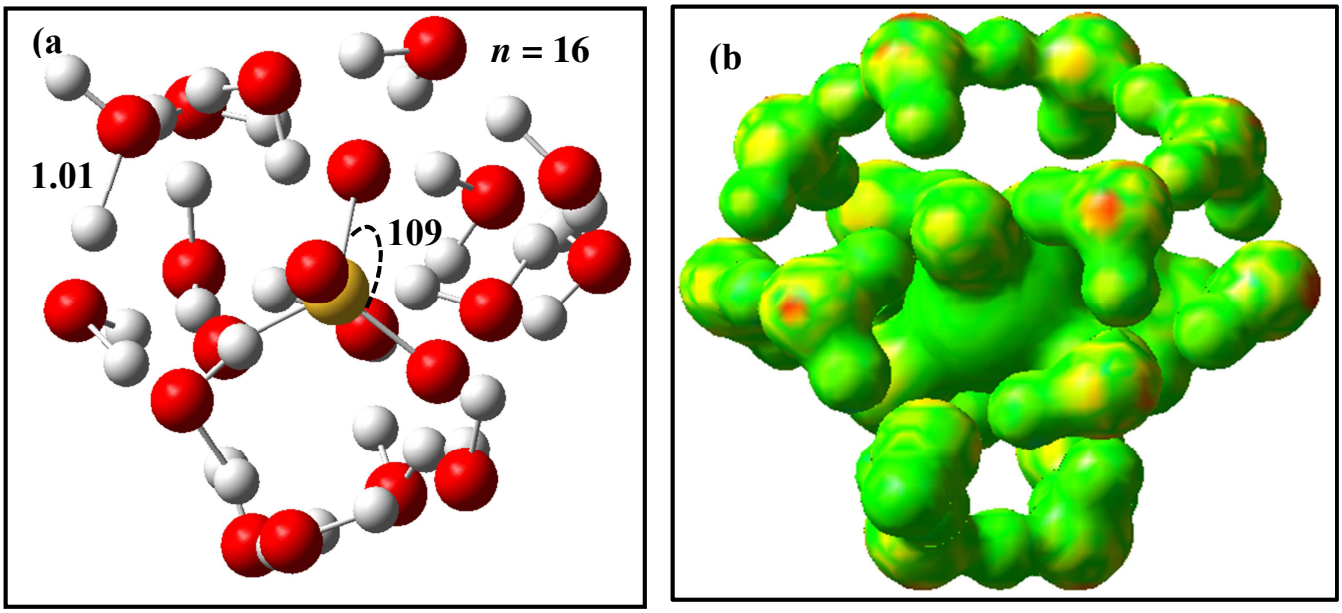


Figure 6. (a) DFT optimized geometry, and (b) Electron density surface (ESP mapping) of $[SO_4^{2-}(H_2O)_{16}]$ ion. For simplicity, formal charge of the sulfate ion is not shown.

region represent alignment of the four oxygen atoms around the central sulfur atom of SO42−. The actual orientation and location of the H2O molecules in the immediate vicinity of SO42− are also depicted where electron density surface of the nearby H2O molecules are seen to be just connected each other, reassuring high chance of forming H−bond between H2O molecules. This electron density model of the hydrated ion also speculates the binding state between SO42− and 16H2O molecules. Except these highlighted abnormalities in the [SO42−(H2O)16] cluster, no other significant distortions are found in the original tetrahedral geometry of the central SO42− ion though small elongation in the S−O bonds (increased to 1.7Å from original 1.5Å) is observed.

3.2 Ground state electronic energy

The DFT computed ground state electronic energies of all the aforementioned hydrated clusters are summarized in Table 1. For simplicity, the comparative electronic energies are also calculated and presented in the third column of the same table. The change in electronic energy versus change in hydration number (n) in the [SO42−(H2O)n] cluster is sketched in Figure 7, which clearly indicates that greater the hydration number (n), the more stable is the sulfate ion. This theoretical observation is in good agreement with the large angle X-ray scattering (LAXS) and quantum mechanical charge field molecular dynamics (QMCF MD) simulation data [26] which reveal that the sulfate-water clusters with an average coordination number of up to 12 and ~11 water molecules respectively, would be more stable than other smaller clusters. Unfortunately, [SO42−(H2O)n] n = 11, 12 clusters are not optimized here by the DFT method due to resource imitations. Moreover, the photoemission spectroscopy [20] and FTIR [21] investigations show that sulfate ions form a hydration shell that consists of a symmetrical dodecahedral arrangement of 16 water molecules and beyond n =16, there is an obvious change in properties of their aqueous solutions. This is the reason, why [SO42−(H2O)16] was chosen as a representative sulfate-water cluster among many larger clusters in the present study. However, the mean SO42− hydration number determined by Raman spectroscopy [27] is only 12 at 0.1 M sulfate solution which is proved later that such lower value shows the properties of incomplete nature of hydration. Hence, the exact size of the most stable hydrated sulfate cluster is still in scientific debate. As a whole, the variation in ground state electronic energy with hydration number clarified that sulfate ions in aqueous solution always intend to exist in their stable forms and for this, they attract large number of oppositely charged poles of water molecules in their immediate vicinity even if they are less in number. The same is applicable to other ions in the Hofmeister series of anions: SO42− > HPO_4^{2-} > CH_3COO^- > Cl^- > NO_3^- and, cations: Mg^{2+} > Li^+ > Na^+ = K^+ > $NH4^+$.

Thermodynamically, the ion hydration process is also an obvious process as it involves multiple steps including cavity formation in the water to make space for sulfate ions (both entropically and enthalpically unfavorable), ions separation from the bulk (enthalpically unfavorable), and finally entering ions into the cavity resulting a strong water-sulfate ion interactions in the newly formed sulfate-water clusters (both entropically and enthalpically favorable), making the overall process of hydration thermodynamically favorable. The detailed thermodynamic analysis can be done only by modeling water-sulfate ions interaction as reactions [28].

Table 1. Summary of the DFT computed ground state electronic energies with increase in hydration number *n*.

Hydration number (*n*)	**Electronic energy *(Hartrees)***	**Comparative electronic energy *(Hartrees)***
1	-775.4097111	0.0000
2	-851.8803785	-76.4707
3	-928.3013495	-152.8916
4	-1004.731702	-229.3220
16	-1895.851365	-1120.4417

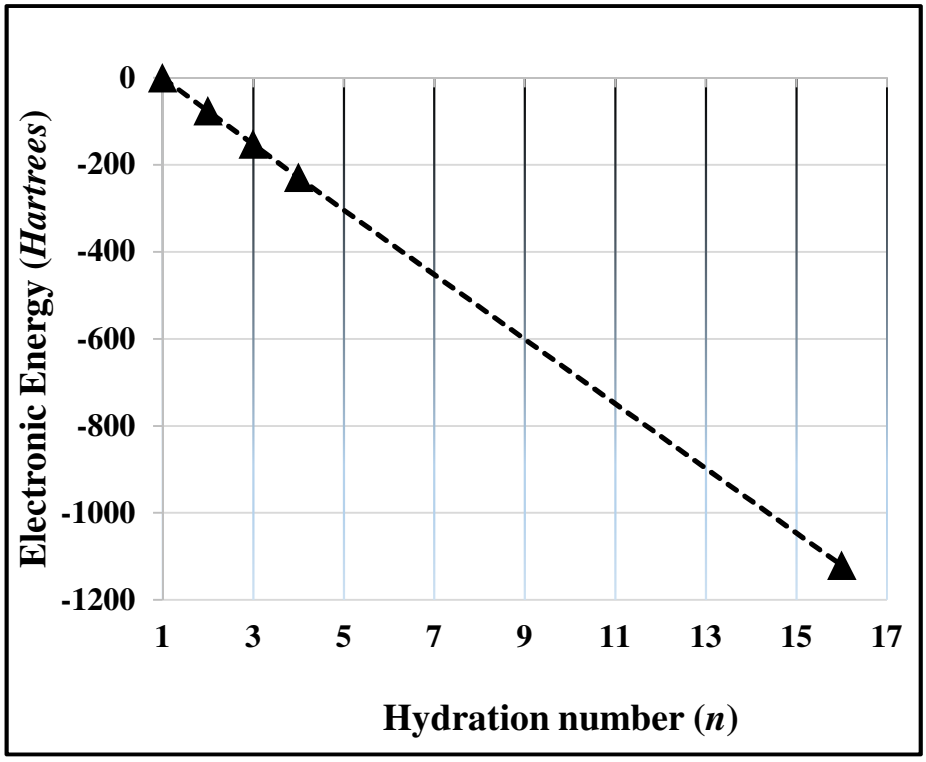


Figure 7. Change in electronic energy of the hydrated sulfate ion clusters with hydration number *n*. For simplicity, comparative values of the electronic energies (3rd column of Table 1) are plotted.

IV. Conclusion

In order to get a clear picture of stepwise hydration and structural stabilization of the divalent SO42− anion that has a strong ability to decrease protein solubility and is ranked first among the anions in the Hofmeister series, an ab initio type theoretical model is applied here to hydrated and unhydrated SO42− ions of the form [SO42−(H2O)n], n ≥ 0. Though many hydrated clusters of the SO42− ion [SO42−(H2O)n], n ≤ 50 are reported in literature, this study is only limited to the unhydrated [SO42−(H2O)n], n = 0; smaller hydrated clusters: monohydrated [SO42−(H2O)n], n = 1; dihydrated [SO42−(H2O)n], n = 2; trihydrated [SO42−(H2O)n], n = 3; and tetrahydrated [SO42−(H2O)n], n = 4; and a comparatively bigger hydrated cluster: dohexahydrated [SO42−(H2O)n], n = 16. The DFT derived electronic structure of the naked SO42− i.e. [SO42−(H2O)0] ion is found to be perfectly tetrahedral in shape, which delocalizes its electron density resulting stable resonance hybrid structure (Figure 1). Thus, the bond lengths measured in the resultant resonance structure are the average of the bond lengths in the separate resonating contributors. Whenever first water is solvated in the immediate vicinity of SO42−, both are found to be bound strongly by forming two strong H−bonds (Figure 2). In a similar way, the second, third, and fourth H2O are also found to form two strong H−bonds each with SO42− (Figure 3-Figure 5). Therefore, in the [SO42−(H2O)4], each oxygen of SO42− is bonded to two H2O and forms a symmetric hydrated cluster (Figure 5). If the solvent number increases from four (n > 4), the negative charges on SO42− may be blocked sufficiently so that single H−bond and H2O−H2O interactions are favored. It is clarified by the DFT optimized geometry of one of the representative bigger clusters i.e. [SO42−(H2O)16] (Figure 6(a)), though the H−bonds formed between H2O and central SO42− ion and H2O and H2O are not shown there for simplicity. While measuring the intermolecular space between the H2O molecules and the space between the central SO42− ion and H2O molecules, they are found to be

so close to each other that the H−bonds formation is a must. This conclusion is made by carefully observing the electrostatic potential map of [SO42−(H2O)16] (Figure 6(b)) where the electron density between the H−bonded species are just in touch to each other. In terms of the structural distortions of the central SO42− ion in all the DFT optimized hydrated clusters, no any significant differences in the O−S−O bond angles and S−O bond lengths are observed except little delocalization of negative charges from central SO42− to surrounding H2O molecules, which is essential while binding them each other to achieve a structural unity.

As a whole, the main conclusions are: whenever the solvent number is in between one to four H2O, the two negative charges on SO42− attract water strongly enough that two H−bonds are formed with each water, and whenever the solvent number exceeded four (while referring to [SO42−(H2O)16]), the negative charges on SO42− may be sufficiently screened so that single H−bond, and H2O−H2O interactions are favored. The author of this article has believed that this computational study will not only ease to understand most of the physicochemical properties of SO42− ions in any inorganic sulfate solutions (including in human body fluids), but also to model their hydrated systems while exploring solvation dynamics in bulk solutions.

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